

Polanyi Evaluation of Adsorptive Capacities of Commercial Activated Carbons

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Commercial activated carbons from Calgon (207C and OVC) and Cabot Norit (RB2 and GCA 48) were evaluated for use in spacecraft trace contaminant control filters. The Polanyi potential plots of the activated carbons were compared using to those of Barnebey-Cheney Type BD, an untreated activated carbon with similar properties as the acid-treated Barnebey-Sutcliffe Type 3032 utilized in the TCCS. Their adsorptive capacities under dry conditions were measured in a closed loop system and the sorbents were ranked for their ability to remove common VOCs found in spacecraft cabin air. This comparison suggests that these sorbents can be ranked as GCA 48 > 207C, OVC > RB2 for the compounds evaluated.

Nomenclature

<i>ECLS</i>	=	environmental control and life support
<i>FTIR</i>	=	Fourier transform infrared radiation
<i>ISS</i>	=	International Space Station
<i>KSC</i>	=	Kennedy Space Center
<i>LMSC</i>	=	Lockheed Missiles and Space Company
<i>TCCS</i>	=	trace contaminant control system
<i>VOC</i>	=	volatile organic compound
<i>A</i>	=	adsorption potential (mol-K/ml)
<i>atm</i>	=	pressure unit, atmosphere
<i>C_e</i>	=	equilibrium chamber concentration
<i>C_{init}</i>	=	initial chamber concentration
<i>C</i>	=	chamber concentration
<i>d</i>	=	diameter
<i>h</i>	=	hour
<i>l</i>	=	length
<i>L</i>	=	liter
<i>min</i>	=	minute
<i>mg</i>	=	milligram
<i>ml</i>	=	milliliter
<i>mol</i>	=	mole
<i>P</i>	=	contaminant partial pressure (atm)
<i>P_s</i>	=	contaminant saturated vapor pressure (atm)
<i>ppm_v</i>	=	part per million by volume
<i>q</i>	=	contaminant adsorptive capacity (ml/g)
<i>T</i>	=	temperature (Kelvin)
<i>V_m</i>	=	contaminant molar volume at normal boiling point (ml/mol)

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α	=	constant
β	=	constant
μmol	=	micromole
μl	=	microliter

I. Introduction

ACTIVATED carbon beds are used for controlling trace contaminants produced by metabolic processes and material offgassing in spacecraft cabin air. In the 1970's, a rapid method based on the Polanyi adsorption potential theory was developed by the Lockheed Missiles and Space Company (LMSC) for predicting the adsorption equilibrium capacities of activated carbons from commonly available adsorbent and adsorbate properties.¹ The Polanyi adsorption potential theory is useful for sizing and accurately predicting the lifetimes of carbon beds used in environmental control and life support (ECLS) systems. This approach has been successfully used for designing Trace Contaminant Control System (TCCS) beds for both Spacelab and International Space Station (ISS) programs. Recently, a test rig for measuring Polanyi plots was constructed. These measurements were validated by reproducing Polanyi plots of ethanol adsorption by Barnebey-Sutcliffe Type 3032 activated carbon collected by LMSC.² Barnebey-Sutcliffe Type 3032 is a commercially obsolete (no longer manufactured) treated carbon used in the TCCS on ISS.

In this paper we compare the efficacy of candidate activated carbons for use in the TCCS using Polanyi plots measured in our test rig. Four untreated activated carbons were chosen as potential replacements of Barnebey-Sutcliffe Type 3032 because they target low concentration volatile organic compounds (VOCs): Calgon 207C, Calgon OVC, Cabot Norit RB2, and Cabot Norit GCA 48. Calgon OVC and 207C are granular activated carbons made from coconut shell by high temperature steam activation. Cabot Norit RB2 is a steam activated extruded carbon with a particle diameter of 2 mm. Cabot Norit GCA 48 is a granular activated carbon produced from coconut shells by steam activation. Cabot Norit GCA 48 was recently selected for removal of volatile methyl siloxanes on ISS because of its high capacity for removal of hexamethyl-cyclotrisiloxane in the presence of an ersatz of ISS VOCs and for its low pressure drop.³

These comparisons are useful for ranking replacements with similar performance characteristics in order to mitigate commercial obsolescence, which arises as commercial products are discontinued, or for evaluating newly released commercial activated carbons.

II. Materials and Methods

The following discussion presents the concept of adsorption potential and describes the experimental method.

A. Polanyi Potential Plots

The adsorptive capacity, q , is determined under closed loop dynamic test conditions whereby the sorbent is exposed to an initial contaminant concentration in a sealed chamber and allowed to adsorb until an equilibrium concentration is reached. The test rig and methodology for obtaining the Polanyi potential plots is described elsewhere.² Briefly, the potential plot relates the adsorption capacity, q , with the adsorption potential, A . The adsorption capacity is defined by Eq. 1 and the adsorption potential is defined by Eq. 2.

$$q = \alpha e^{-\beta A} \quad (1)$$

$$A = (T / V_m) \log_{10} (P_s/P) \quad (2)$$

In Eq. 1, empirical constants (α and β) are determined from the adsorption potential plot. In Eq. 2, T is the sorbent temperature (K), V_m is the molar volume at the normal boiling point (ml/mol), P_s is the contaminant vapor pressure (atm) at T , and P is the contaminant partial pressure (atm) obtained from the equilibrium concentration. The adsorption potential is calculated from the molar volume, the vapor pressure, and the equilibrium concentration.¹ The Polanyi adsorption potential theory has been applied to the study of activated carbon adsorption for VOCs.^{4, 5}

B. Closed Loop Apparatus

The system consists of a 14-liter mixing volume, which includes the 0.4-liter cell of a Gasmet DX-4030 Fourier transform infrared radiation (FTIR) spectrometer (Figure 1). The system also includes a diaphragm pump to recirculate the test gases, a fan to mix the test gases, and a bypass line with valving to divert the test gases through tube containing the adsorbent.² A sample (4 mm diameter x 20 mm long; 40-60 mg dry sorbent) is placed in a thermal desorption tube and fed with a single VOC in the mixing volume.

C. Sample preparation

The adsorbent particles are large compared to the 4 mm desorption tube so they are crushed into 2-3 mm pieces in a pestle. Powder formed during crushing was not used. The desorption tubes are loaded with enough activated carbon to ensure that the l/d (length/diameter) ratio is near 5.

The adsorbent samples must be dried prior to use because they adsorb water vapor during storage. A weighed sample (40-60 mg) as received is loaded into the 4mm ID desorption tube and held in place using 2 glass wool plugs. The loaded tube is weighed and heated to 100°C with a flow rate of 100 ml/min of N₂ in a desorption tube conditioning oven (Scientific Instrument Services, Inc). This dries the adsorbent and removes moisture adsorbed during storage and transport to the Kennedy Space Center (KSC). The loaded tube is weighed after 1 h and after 2 h, until its mass is constant. The mass difference is ascribed to water and subtracted from the initial sample mass.

D. Measuring equilibrium loading capacities

The sealed mixing volume is loaded with a single VOC (ethanol, acetone, dichloromethane, or toluene) using an adsorbent tube injection system (Supelco ATIS) that flash vaporizes a 7 – 10 µl sample into a continuous flow of an inert gas which carries the sample into the chamber.² Once loaded, the VOC circulates through the desorption tube and returned to the mixing volume until the equilibrium concentration is reached. The initial concentration, C_{init} (ppm_v) is recorded before circulating the VOC mixture through the adsorbent sample. The change in concentration in the mixing volume is measured every 20 seconds using the FTIR until an equilibrium concentration, C_e (ppm_v), is reached. When the ratio C_e/C_{init} becomes constant, the chamber concentration, C_e , is in equilibrium with the contaminant concentration in the adsorbed phase in the activated carbon. The Polanyi adsorption potential and the equilibrium adsorptive capacity, q , (ml/g) is derived based on data acquired at this condition. The system used for the present evaluation was found to leak, thus a correction was applied to the adsorption data.²

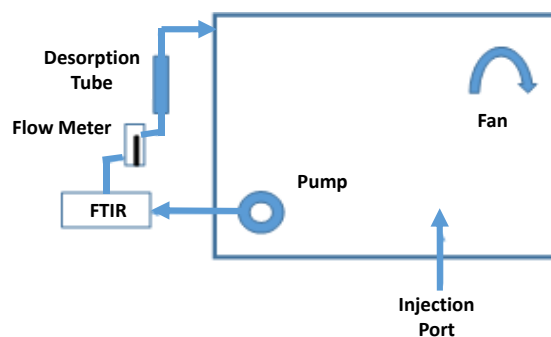


Figure 1. A simplified schematic of the closed loop adsorption equilibrium system. The mixing chamber is dosed with a known VOC quantity and then circulated through the FTIR and sorbent tube.

III. Results

Results pertaining to adsorption potential plots for four commercially-available, untreated, activated carbons are presented. The closed loop equilibrium adsorption capacity apparatus was used to acquire equilibrium adsorption capacity data for acetone, ethanol, dichloromethane and toluene to construct adsorption potential plots. Figure 2 includes the LMSC data for the 10% phosphoric acid treated Barnebey Sutcliffe Type 3032 and the untreated Barnebey-Cheney Type BD activated carbons for comparison.¹ The Barnebey-Cheney Type BD activated carbon has a higher equilibrium adsorption capacity than Barnebey-Sutcliffe Type 3032, it lacks the NH₃ removal capacity imparted by the acid treatment, and was used as a baseline for the untreated adsorbents tested.

E. Comparison of Activated Carbons

The VOC equilibrium capacities of four commercially-available activated carbons was evaluated (Figure 1). Calgon OVC and 207C had

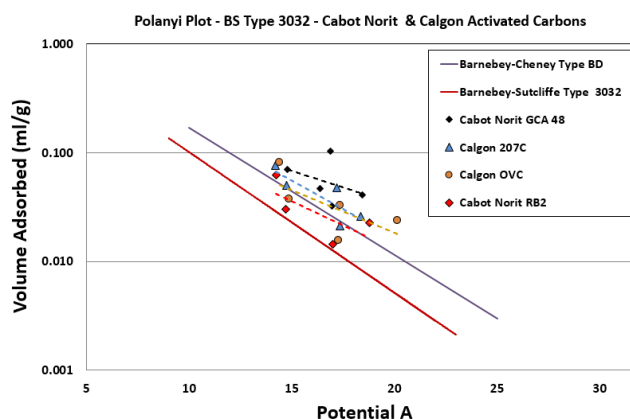


Figure 2. Polanyi adsorption potential plots for Calgon & Cabot Norit Carbon activated carbons. This comparison suggests that CGA 48 > OVC, 207C > RB2, Barnebey-Cheney Type BD > Barnebey-Sutcliffe Type 3032 for the compounds evaluated under dry conditions.

similar equilibrium adsorptive capacities to each other and to that of the untreated Barnebey-Cheney Type BD activated carbon. The equilibrium adsorptive capacity of Cabot Norit RB2 was lower than that of Calgon OVC, Calgon 207C, and Barnebey-Cheney Type BD activated carbons. In contrast, Cabot Norit GCA 48 is a better sorbent than Calgon OVC, Calgon 207C, Barnebey-Cheney Type BD, Barnebey-Sutcliffe Type 3032 activated carbons for the compounds evaluated.

IV. Discussion

The Polanyi adsorption potential methodology serves as the framework for characterizing equilibrium adsorption capacities of candidate activated carbons for controlling trace contaminants in spacecraft cabin air. This approach has been utilized in sizing TCCS beds for the Spacelab and ISS programs. Adsorption potential characteristic curves are not only useful for adsorbent bed design but also for comparing candidate sorbent replacements for commercially-obsolete adsorbent media used for the ISS TCCS.

A closed loop method was used to measure the equilibrium adsorptive capacities of four untreated activated carbons under dry conditions: Calgon OVC, Calgon 207C, Cabot Norit RB2, and Cabot Norit GCA 48. These activated carbons differ in their composition and in the method used for activation, which may cause differences in their adsorptive capacities for VOCs. The activated carbons were crushed so that small samples could be used for the purpose of reducing test duration. Crushing increases the surface area and may affect kinetics of adsorption in flow through methods where mass transfer coefficients matter. In this method, the adsorbent is exposed to the single VOC until its pores reach equilibrium so crushing the samples is not expected to affect equilibrium capacity.

The adsorptive capacities of these activated carbons were compared to that of Barnebey-Cheney Type BD, an untreated activated carbon with an improved equilibrium adsorptive capacity than acid-treated Barnebey-Sutcliffe Type 3032 utilized in the TCCS. This comparison suggests that these sorbents can be ranked as GCA 48 > 207C, OVC > RB2, Barnebey-Cheney Type BD > Barnebey-Sutcliffe Type 3032 for the compounds evaluated.

V. Future Work

The assumption that crushing the samples does not affect equilibrium capacity should be investigated. The equilibrium adsorptive capacity measurements should be repeated using humid gas streams because TCCS beds are used in the presence of water vapor, which may alter the vapor adsorption of VOCs by activated carbon.⁶ Including the effect of water vapor would be useful in the design of adsorption systems utilizing activated carbon for the removal of VOCs from spacecraft cabin air.

Acknowledgments

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